MODIFIED CARBON SUBSTRATES FOR ELECTROCATALYTIC OXIDATION OF SELECTED HETEROCYCLIC CARBINOLS

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ABSTRACT

Electrochemically modified carbon based substrates are used as electrodes for electrocatalytic oxidation of different heterocyclic carbinols. Carbon fiber paper (CFP) is used as the electrode substrate on which various modifications are employed. Modified electrodes were prepared by using different surface modification strategies such as electrodeposition of Pd nanoparticles or Pd-Pt bimetallic nanoparticles on a conducting polymer, polyaniline which is electropolymerized on to CFP. Biomass derived porous carbon nanoparticle coated CFP was also used for electrodeposition of Pd nanoparticles or MnO_2-Pi nanoparticles. Such modification methods have attracted a lot of attention due to their exceptional stability, high electronic conductivity, mechanical strength, and good adhesive property for the substrate to the modified electrode. The modified electrodes exhibit excellent electrochemical and physicochemical properties which are demonstrated using various analytical techniques. The organocatalytic reagent, TEMPO is used as a mediator throughout the study which helps to carry out the oxidation in an aqueous acidic medium. The developed electrodes have been successfully applied for the oxidation of different heterocyclic alcohols such as 4-pyridinemethanol, 2-thiophene methanol, and 2-Furfuryl alcohol.

Keywords: Electrocatalytic oxidation, electrical conductivity, TEMPO, Heterocyclic alcohol, porous carbon.

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1. Introduction

Electroorganic chemistry is a multidisciplinary science that includes the fields of organic chemistry, biochemistry, physical chemistry, and chemical engineering. Electroorganic synthesis is recognized as an environmentally benign methodology for the oxidation and the reduction of organic compounds, since dangerous and toxic redox reagents are replaced by electric current, and the overall energy consumption is reduced [1]. Although the electrochemical step is usually one part of a multi-step sequence, it constitutes a key process for the generation of a variety of reactive intermediates [2]. Also, it provides a means whereby unstable or hazardous reagents can be produced in situ and allows reactions to be carried out under mild conditions [3]. Electrodes that are considered heterogeneous catalysts can be easily separated from the products. Supporting electrolytes and electrochemically active intermediates may be regenerated electrochemically and recovered easily. Today cyclic voltammograms are often used to define the redox properties of newly synthesized organic compounds. Similarly, the structural characterizations of these newly synthesized compounds are done with the help of IR and NMR spectra. Electroorganic chemistry often provides interesting and useful alternatives to conventional synthetic methods that fail in obtaining selectivity of the product formation and constitutes a useful tool for the organic chemist. With numerous applications on the laboratory scale [4] and several applications in the industry [5], organic electrosynthesis can be regarded as a very versatile field of organic synthesis. The significance of this method is the reduced number of steps to reach products from reactants, the use of cheaper starting materials, and the absence of hazardous reagents. These methods hold a prime position in the field of synthetic organic chemistry.

Heterocyclic compounds constitute the largest and most varied family of organic compounds, significant to almost all aspects of modern organic chemistry, medicinal chemistry, and biochemistry. Heterocyclic alcohols are precursors in the manufacture of heterocyclic aldehydes. These aldehydes and their derivatives have a wide range of applications. Heterocyclic aldehydes are used as core substrates for the manufacture of veterinary products, drug molecules in pharmaceutical industries, dyestuffs, sanitizers, agrochemicals, antioxidant supplements, corrosion inhibitors, pesticides, and antidotes [6]. They are also used as carriers for the synthesis of other organic compounds, antibiotics, and alkaloids. Oxygenation of heterocyclic alcohols for the synthesis of derivatives of heterocyclic aldehydes is of great importance due to their significant

role as chemical intermediates in pharmaceutical industries. Conventional synthesis of these intermediates has disadvantages such as low atom economy and accumulation of a large amount of waste. Traditional methods for the synthesis of heterocyclic aldehydes involve, oxidation of primary alcohols to aldehydes then to carboxylic acids, can be carried out by using potassium permanganate ($KMNO_4$), potassium dichromate ($K_2Cr_2O_7$), Pyridinium chlorochromate (PCC), and Pyridinium dichromate (PDC). This reaction cannot stop at the aldehyde stage directly as hydroxyl groups are converting to carboxylic groups and are exothermic, toxic, carcinogenic, and rarely oxidizes unsaturated bonds [7-9]. In the present investigation, different modified electrodes have been used to convert heterocyclic carbinols to the corresponding heterocyclic carbinals.

Carbon-based electrodes have found widespread use in electrochemistry due to their broad versatility and low cost amongst other advantages. Various carbon-based electrodes such as carbon paste electrode (CPE), glassy carbon electrodes (GCE) carbon fiber paper (CFP), etc. have received great attention as they are advantageous in terms of renewability, stable response, low ohmic resistance non-requirement of internal solutions [10] and including good electrical conductivity, chemical inertness, and wide potential range. CFP offers abundant reduction and oxidation reaction sites due to high porosity and wettability. On modification, the conductivity and electroactive surface area tend to increase significantly [11]. Therefore, we have chosen CFP as the working substrate electrode. Chemical modifiers like conducting polymers can be introduced onto the surface of the electrode by electrochemical methods to improve the catalytic efficiency thereby achieve a better yield. These polymers comprise carbon, hydrogen, and heteroatoms (oxygen, nitrogen, sulfur) and contain π-conjugation across the polymer backbone. Conducting polymers (CPs) such as polyacetylene (PA), polyaniline (PANI), polyparaphenylene (PPh), polypyrrole (PPy), polythiophene (PTh) and poly(3,4-ethylenedioxythiophene) (PEDOT) provide good conductivity and are most sought-after supporting catalyst materials. The inherent conductivity of these CPs results from the formation of polarons (radical cations) and bipolarons. In electrochemical polymerization, the radical-radical coupling leads to the formation of a radical dication. This loses two protons to form a neutral dimer, which can be oxidized to a radical cation and reacts further to form the polymer [12]. Perhaps an adherent polymer film can be grafted directly onto an electrode surface in one simple step. Reproducible films can be obtained as the film thickness can be controlled by monitoring the charge passed during deposition and the

polymer films formed have fewer impurities as harsh oxidizing agents are not used. Improved electrical conductivity, mechanical strength, and adhesive property to the substrate are important advantages offered by CPs thereby making them very useful in various applications. Electropolymerization of conducting polymers on a substrate electrode induces porosity and roughness due to their three-dimensional growth on the substrate, which enhances the surface area of CFP substrate [13]. This favors electrode-electrolyte interfacial properties for various electrochemical reactions, wherein CPs transfer electrons between electrode and dispersed metal nanoparticles along the chains of the polymer. As a result, metal nanoparticles immobilized on CP substrates prevent agglomeration of nanoparticles. Therefore, electrooxidation or electroreduction efficiency can be improved by introducing metal nanoparticles into the porous conducting matrices, which in turn increases the surface area [14].

Carbon-based materials for electrode modification such as diamond, nanotubes, nanofibers, graphene, activated carbon, and nanospheres have triggered substantial interest in developing various energy conversion devices owing to their low density, specific and high surface areas, and high flexibility along with their increased stability and mechanical strength [15]. Among these listed materials, carbon nanospheres (CNSs) are attractive candidates for developing functional materials to be applied in different areas of modern science and technology due to their simple production methods, regular surface morphology, uniform particle size, high specific surface area, good dispersion properties, low toxicity, high chemical and thermal stability, large packing density, high porosity, excellent biocompatibility with electronic and ionic conductivities [16]. Earlier, CNSs were synthesized from graphite powder, coal, petroleum products, polymers, and liquid/gaseous hydrocarbons, but these precursors have become scarce and impact the environment negatively. Therefore, the vital need to explore carbon materials from environment-friendly and cost-effective carbon precursors led to utilizing natural resources for the production of CNS. Natural resources such as plant biomasses, agriculture bio-wastes, and hydrocarbons are ample, massive, and diversified and can act as renewable carbon precursors. Remarkably, CNSs have been synthesized by using carbon precursors (e.g., hemicelluloses and lignocelluloses) present in some of the natural resources such as rice husks, mango leaves, banana stem, onion peel, banana fibers, apricot shell, corn grain, coconut shell, sago bark, and bamboo. The natural lignocellulosic components have gained considerable attention due to their high availability, low cost, and low

toxicity. Therefore, CNSs derived from natural resources have been utilized for several applications. Generally, carbon materials are synthesized by chemical vapor deposition (CVD), nanocasting methods, electric arc discharge technique, and carbonization of sugars, polymeric aerogels, and MOFs [17]. The requirement of harsh and energy-demanding synthetic conditions makes these methods disadvantageous. CNSs prepared from areca nut, monkey pods, and sago barks were used for the modification of electrodes as these are environmentally clean, and cost-effective materials.

Electrochemically deposited metal nanoparticles on conducting polymers/carbon nanospheres host matrices have received great attention for various applications such as sensors for biological systems, supercapacitors, corrosion protective coatings, and electrocatalysts [18,19]. Immobilization of noble metal nanoparticles on an active matrix may enhance the overall reactivity of the catalytic metal centers and prevents agglomeration of the nanoparticles, thereby improving the catalytic efficiency due to an increase in the electroactive surface area of the electrode [20]. The activity of noble metal-based electrocatalysts depends on their dispersion. Electrochemical formation of mono/bi-metallic electrocatalysts on the host matrix layer has been reported for the electrocatalytic oxidation of formic acid, methanol, ethanol, benzyl alcohol other organic molecules, and sensing of some organic and inorganic analytes [21]. Reports are not available for the dispersion of noble metal nanoparticles on CNSs thin films for the oxidation of heterocyclic carbinols. Also, the aggregation of nanoparticles due to high surface energy could be overcome by employing carbonaceous support materials like CFP as they are good matrices for immobilization of CNSs and nanoparticles.

Electrochemical organic synthesis comprises promising environment-friendly approaches when compared to conventional organic synthesis owing to the use of electrons as reagents rather than conventional toxic reagents. With the use of electrons as the reagent, transformations can be carried out either directly or indirectly [22, 23]. As a substitute to conventional oxidants, stable nitroxyl radicals have received great attention for application as oxidation catalysts. One of the most prominent representatives of the nitroxyl radicals was found to be 2,2,6,6- Tetramethylpiperidinyl-l-oxyl (TEMPO). The remarkable feature of TEMPO is its stability in aqueous and non-aqueous media due to the presence of steric hindrance around the nitroxyl moiety. The organocatalytic reagent, TEMPO is a highly active and stable compound that is extensively utilised in the selective

oxidation of primary alcohols to generate aldehydes and also holds the potential to be used as mediators in several oxidation reactions [24]. An acidic medium is necessary to make the catalytic system effective; the oxoammonium salt ($TEMPO^+$) is formed by the disproportionation of TEMPO catalyzed by the acidic medium [25]. TEMPO can be reversibly oxidized by electrochemical methods or employing oxidants such as H_2O_2, O_2, and metal halides, to generate an active oxoammonium species ($TEMPO^+$), which can be obtained by a chemical or electrochemical one-electron oxidation of TEMPO. This species is an ideal oxidant for selective oxidation of alcohols to corresponding aldehydes or ketones without undergoing over-oxidation forming acids [26]. Generally, a three-electrode system including a working electrode, in which the oxidation or reduction process occurs, a reference electrode such as SCE (Saturated calomel reference electrode) or silver-silver chloride electrode and an auxiliary or counter electrode, which carries bulk current can be used. Surface modification of the electrodes with suitable substances may improve and enhance the catalytic reactivity.

Electrocatalytic oxidation of different heterocyclic carbinols to their corresponding heterocyclic aldehydes using TEMPO medium is studied by employing different modified electrodes. This ensured good to excellent yields of the products for electrooxidation of alcohols by using modified carbon fiber paper electrodes. Selected heterocyclic carbinols such as 4-pyridyl carbinol, 2-thiophene carbinol and2-Furan carbinol are used for the electrooxidation to yield 4-pyridyl carbinal, 2-thiophene carbinal, and 2-Furan carbinal respectively and the product formation is confirmed by using different spectroscopic techniques.

2. Review of Literature

Among various synthetic methods reported for the oxidation of organic compounds, electrochemical techniques have gained momentum due to their ease of operation, rapid response, and high sensitivity. The electrochemical method of oxidation possesses advantages like ease of fabrication, high electroactive surface area, voltammetric performance, and enhanced electrochemical activity [27]. Surface modification of electrodes by conducting polymers, carbon nanospheres, and metal nanoparticles on the substrates is a very efficient approach to reach enhanced current responses and obtain an interface with a highly specific binding affinity to the desired molecule. Based on an extensive literature survey, synthetically important molecules such

as pyridyl carbinol, thiophene methanol, and furfuryl have been chosen as the reactants of interest for electrocatalytic oxidation.

The oxidation of alcohols to corresponding carbonyl compounds is an important transformation in organic chemistry and one of the important functional group conversions in synthetic chemistry. However, the oxidation of heterocyclic carbinols to aldehydes electrochemically constitutes a novel and efficient alternative method over the conventional methods. The product, heterocyclic carbaldehydes are important raw materials in the field of pharmaceuticals, dyestuffs, perfumes, cosmetics, and the food industry.

Generally, carbinals are synthesized by selective liquid-phase oxidation of corresponding heterocyclic methanols using catalysts such as MnO_2, lead tetraacetate, and SeO_2 [28]. Although these catalysts were found to be reasonably good for the preparation of heterocyclic aldehydes resulting in moderate yields, they possess major limitations in terms of toxicity, large volume requirement, non-regenerability of the catalyst, and inability to convert large amounts of carbinols to carbinals. The conventional synthesis of these heterocyclic intermediates by oxidation of methyl pyridine, thiophene nitriles, methyl thiophene, furfuryl alcohols, and pyridine methanols involve nucleophilic substitution by formylation reaction on the heterocyclic ring [29]. Formylation reactions of heterocyclic compounds were carried out by various methods such as the Gatterman-Koch reaction, Vilsmeier-Haack reaction, and Rieche formylation [30]. These methods have disadvantages like low atom economy and accumulation of a large number of by-products and toxic compounds, usage of poisonous gas and gaseous reactants demanding the use of high-pressure devices. Another important method for the oxidation of heterocyclic methanols and alkyl substituted heterocyclic compounds involves the use of oxidizing agents such as $KMNO_4$, $K_2Cr_2O_7$, Pyridinium chlorochromate (PCC), and Pyridinium dichromate (PDC)[7-9]. Limitations of these methods include the inability to stop the oxidation at the aldehydic stage as it generally tends to convert -CH_2OH group directly to -COOH group, exothermic nature of the reaction, and carcinogenic by-products.

Use of stoichiometric reagents such as V^{5+}/V4+, permanganate, Mn^{3+}/Mn^{2+}, hypervalent iodine compounds, and Ce(III)/Ce(IV)- redox mediator/catalysts were reportedly effective in the indirect conversion of alkyl derivatives of heterocyclic compounds to aldehydes [31]. These types of metal-based oxidation reactions may leave traces of toxic heavy metals in the products. Also, oxidation

reactions are usually carried out in a halogenated organic solvent medium which is not environment friendly. The production of medicinally important heterocyclic carbinals with the use of eco-friendly oxidants, with high selectivity and good yield in a single step, remains a challenge for organic chemists till date. Therefore, the development of a more sustainable, environmentally benign, clean, efficient, and facile synthetic approach for heterocyclic aldehydes by using novel catalytic materials instead of toxic oxidants is in great demand.

The electrochemical reactions of the substrate with mediators may be carried out in the in-cell or ex-cell method. In the latter case, the electrochemical reaction is carried out in a separated vessel and the mediator is recycled back to the electrolytic cell for regeneration. Nitrate mediated selective oxidation of alkyl aromatics by emulsion electrolysis gives the corresponding carbonyl compounds at a moderately high yield. Even though the report claims the method to be inexpensive, the use of 15 cm^2 area of two platinum sheets as electrodes is contradicting the advantage of the system.

Between different conducting polymers, polyaniline (PANI), polythiophene, poly(3,4-ethylenedioxythiophene) (PEDOT), and polypyrrole (PPy) has been widely reported as supporting host matrix for the dispersion of metal nanoparticles [11-13]. Among them, PANI has been immensely researched in sensors [32-35], electrochromic devices [36], supercapacitors [37,38], solar cells [39], antibacterial, batteries [40], catalysis, and corrosion protection coatings. PANI has captured the interest of the scientific community due to its attractive properties, such as high stabilities in air and water, excellent electrical conductivity in its oxidized/protonated form, acid-base properties, electrochromic behavior, and electrochemical capacitance [41], exceptional environmental stability [42], low cost, easy synthesis methods, redox properties associated with the nitrogen atoms in PANI [43], ion-exchange capacity, and tunable chemical properties [44]. Reported literature shows polyaniline is the most widely studied conductive polymer and is readily formed in aqueous solutions on various substrates (mainly inert metals and semiconductors) [45,46], it is used less for the formation of protective coatings on oxidizable metals [47,48]. S. Kumar *et al* used a Glassy carbon electrode modified with silver nanoparticles anchored reused graphene oxide for Methanol oxidation but this work reported as tedious electrode preparation. In another reported work Glassy carbon electrode modified with Pt-Ag coated on porous polyaniline (PANI). Template Attapulgite (ATP) was used for the preparation of porous polyaniline (PANI)

with enhanced surface area and etched with HF acid. This work has excellent electrocatalytic activity, better poison resistance, and good stability towards glycerol oxidation but the electrode preparation involves several steps and it is time-consuming [49].

Carbon-based materials have been used in a variety of practical applications such as energy storage, water purification, catalysis, gas separation, energy conversion, and biomedical applications due to their ability and affinity to absorb organic and inorganic molecules [50]. Carbon nanospheres (CNSs) are highly porous and possess an open-pore network of carbon matrix that facilitate rapid molecular diffusion, dispersion of metal nanoparticles and promote accessibility to the entire pore surface [51,52]. These materials were used as reinforcement substances for anode materials in Na/Li-ion batteries, supercapacitors, energy storage materials and many non-energy applications including novel supports of catalytic systems, adsorbents, cell delivery systems, multiphoton bioimaging, and photoluminescence applications [53,54]. Generally, carbon materials are synthesized by chemical vapour deposition (CVD), nanocasting methods, electric arc discharge technique, carbonization of sugars, polymeric aerogels, and MOFs. The requirement of harsh and energy-demanding synthetic conditions makes these methods disadvantageous. In the present investigation, an environmentally benign, clean, catalyst-free, and economically favourable pyrolysis method was employed for the production of CNSs from biowaste [55-57]. Moreover, CNSs have already been used as materials for electrode assemblies in polymer electrolyte membrane fuel cells (PEMFCs) because of their high surface area and their role in serving as the core for metal nanoparticles [58]. Also, CNSs have been used as electrode materials for fabricating energy storage devices such as supercapacitors [59-62]. However, CNSs are not explored to the fullest for electrocatalytic applications even though their physical and chemical functions are similar to CNTs and graphene.

Carbon-based supports are generally utilised for dispersing the nanoparticles to achieve higher catalytic activity. Palladium nanostructures and nanocomposites are studied intensively because of their significance as catalytic materials, sensors, and hydrogen storage materials [18-19,63]. They have emerged as an effective alternative to Pt for electrooxidation of organic molecules. Bimetallic nanoparticles (NPs) containing two different metal elements have increased electrocatalytic activity and chemical stability, water-insolubility, excellent electronic conductivity, controllable shape and size in comparison with monometallic ones [64]. The catalytic properties of the original

single-metal catalysts can be improved by bimetallic nanoparticles as they can retain the functional features of each component exhibiting significant properties such as increased surface area, promoted electron transfer, and enhanced electrocatalytic activity due to the synergistic effects via cooperative interactions [65,66]. Among the most explored bimetallic nanoparticles, satisfactory electric properties in electroanalysis and electrocatalysis were reported using Pd-Pt nanoparticles in recent years [67,68].

Metal-free mediators for the oxidation of alcohols to the corresponding carbonyl compounds have been receiving increasing attention in organic synthesis [69,70]. Specifically, TEMPO (2,2,6,6-Tetramethylpiperidinyl-l-oxyl) and its derivatives are persistent free radicals widely used in chemistry, biology, and having great industrial interest [71,72]. Substituted nitroxyl radicals are prepared in larger amounts in high yields starting from the inexpensive basic chemicals acetone and ammonia [73]. Additionally, the mediator TEMPO can be easily recovered in quantitative yield after the oxidation reactions [74]. The introduction of TEMPO as a co-catalyst in the transition-metal-based catalytic systems was effective in improving the reaction selectivity under mild conditions. In particular, the redox cycle of TEMPO including the corresponding hydroxylamine (TEMPOH) and oxoammonium cation ($TEMPO^{+}$) forms the basis of many applications such as catalytic oxidation of alcohols or dismutation of superoxide [75].TEMPO is stable in both aqueous and non-aqueous media and this stability is linked to its steric factors and makes the reagent environmentally benign [76]. Although TEMPO has been known to be useful for the selective oxidation of primary alcohols in the presence of secondary alcohols [77]. It has difficulties in catalyzing the oxidation of sterically hindered secondary alcohols. The difficulty in the oxidation of secondary alcohols by TEMPO is associated with the steric environment around the active site [75]. The radical scavenging properties of TEMPO make it a versatile catalyst in biochemical applications.

Based on the extensive literature survey done for electrochemical oxidation of organic compounds, the following research gaps have been identified:

- Need for developing facile electrode fabrication methods
- Demand for an electrochemical method with high selectivity and good yield in a single step for the preparation of heterocyclic carbinals
- Non-availability of methods with high reproducibility and specificity

- ❖ Metal nanoparticles dispersed in conducting polymer matrices are majorly reported for fuel cell oxidation of alcohols and not reported for electrochemical oxidation of heterocyclic carbinols
- ❖ High electrocatalytic efficiency of metal nanoparticles like Pd, bimetallic Pd-Pt, MnO_2-Pi, and PANI, CNSs towards oxidation of organic heterocyclic carbinols are yet to be explored extensively
- ❖ Need for the development of a more sustainable, green, clean, efficient, and facile synthetic approach for heterocyclic aldehydes by using novel catalytic materials instead of toxic oxidants

Therefore, the present study involves the development of the electrochemical method as an efficient synthetic route for the preparation of heterocyclic aldehyde derivatives.

Objectives

The main objectives of the present investigation are as follows

- ❖ To modify the electrode substrate for electrocatalytic oxidation of heterocyclic carbinols
- ❖ To characterize the modified electrode materials by different electroanalytical techniques.
- ❖ To optimize the experimental parameters suitable for the electrochemical oxidation of heterocyclic carbinols.
- ❖ To study the applicability of modified electrodes for the electrocatalytic oxidation of heterocyclic carbinols.

3. Research work carried out

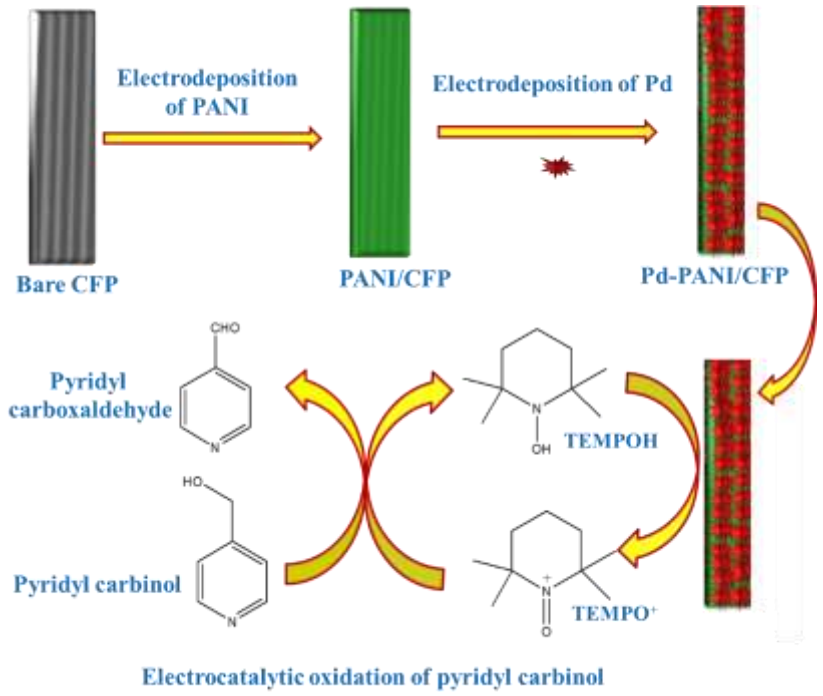
General Methodology

- Construction of chemically modified carbon fiber paper electrodes using various substrates like metal nanoparticles, carbon nanospheres, and conducting polymers.
- Characterization of modified electrodes by SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy), XRD (X-ray Diffraction), XPS, Raman, and FT-IR (Fourier Transform Infrared) analysis.
- Electrochemical studies are performed by using Cyclic voltammetric and electrochemical impedance spectroscopy techniques.

- Optimization of experimental conditions.
- Developed techniques are used for the oxidation of different heterocyclic carbinols.

1. Work 1 - TEMPO-Mediated Aqueous Phase Electrooxidation of Heterocyclic Methanols at Palladium-Decorated PANI on Carbon Fiber Paper Electrode

In this investigation, Pd nanoparticles were uniformly dispersed on the PANI host matrix which was then electrochemically deposited on a carbon fiber paper (CFP) electrode. The electrochemical properties of the modified electrodes were studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The physicochemical properties of the modified electrodes were studied using Scanning electron microscopy (SEM) with Energy-dispersive X-ray spectroscopy (EDS), Transmission electron microscopy (TEM), Optical profilometry, X-ray diffraction (XRD) spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. The modified electrode was successfully used for TEMPO-mediated electrocatalytic oxidation of heterocyclic carbinols in an aqueous acidic medium in the presence of a surfactant. In the present study, we have taken 4-pyridinemethanol also called pyridyl carbinol as the model compound for further studies. The use of TEMPO as a mediator prevents over-oxidation of pyridyl carbinol to the corresponding acid and rather favors the formation of pyridyl carboxaldehyde. The products obtained at the modified electrodes were analyzed by taking the solution obtained after prolonged electrolysis (48 hours) of 10 mM pyridyl carbinol by GC-MS and the isolated product purified by column chromatography was then analyzed by 1H NMR and FTIR spectroscopy. Pd-PANI/CFP electrode has exhibited enhanced electrocatalytic activity towards TEMPO-mediated oxidation of pyridyl carbinol owing to the higher electrochemically active surface area of the modified electrode. Several parameters including the concentration of functional monomer, number of cycles used for the electropolymerization process of conducting polymer, and the effect of scan rate were optimized to obtain the best electrochemical response for the oxidation of pyridyl carbinol. The CV studies suggested higher electrochemical activity for Pd-PANI/CFP electrode when compared to PANI/CFP and bare CFP electrodes towards TEMPO-mediated oxidation of pyridyl carbinol. The proposed work is schematically illustrated in **Scheme 1.**



Scheme 1. Graphical representation for electrooxidation of pyridyl carbinol at Pd-PANI/CFP composite electrode using TEMPO as a mediator.

The cyclic voltammetric behavior of $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ at Pd-PANI/CFP, PANI/CFP, and bare CFP electrodes was studied in 5 mM $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ in 0.1 M KCl using 0.05 Vs^{-1} scan rate (**Figure 1**). The electrochemically active surface area of the electrodes was estimated using CV data obtained for the redox reaction of $[Fe(CN)_6]^4/[Fe(CN)_6]^{3-}$. The anodic peak current was plotted against the square root of scan rates and the respective slopes of the obtained graphs were determined. Randles- Sevcik equation (Equation 1) was used to find out the surface area of the electrode using respective concentration, slopes, and diffusion coefficients.

$$I_p = 2.69 \times 10^5 \, A D_O^{1/2} n^{3/2} v^{1/2} C \qquad (1)$$

Where, A represents the electrochemically active surface area of the electrode in cm^2, D_o is the diffusion coefficient in cm^2/s, n is the number of electrons involved in the redox reaction, v is the scan rate in Vs^{-1} and C is the concentration of $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ in the bulk solution in mol/cm^3. The surface area obtained for bare CFP, PANI/CFP, and Pd-PANI/CFP electrodes was found to be 1.55 cm^2, 2.78 cm^2, and 9.38 cm^2 respectively. It is evident that a larger surface area was obtained for Pd-PANI/CFP electrode than that for PANI/CFP and bare CFP electrodes.

The results revealed that the presence of conducting polymer matrix PANI on CFP provides enhanced catalytic activity due to larger surface area and provides a platform for uniform dispersion of Pd nanoparticles. The substantial increase in the background current observed for Pd-PANI/CFP electrode was in good agreement with the cyclic voltammogram obtained.

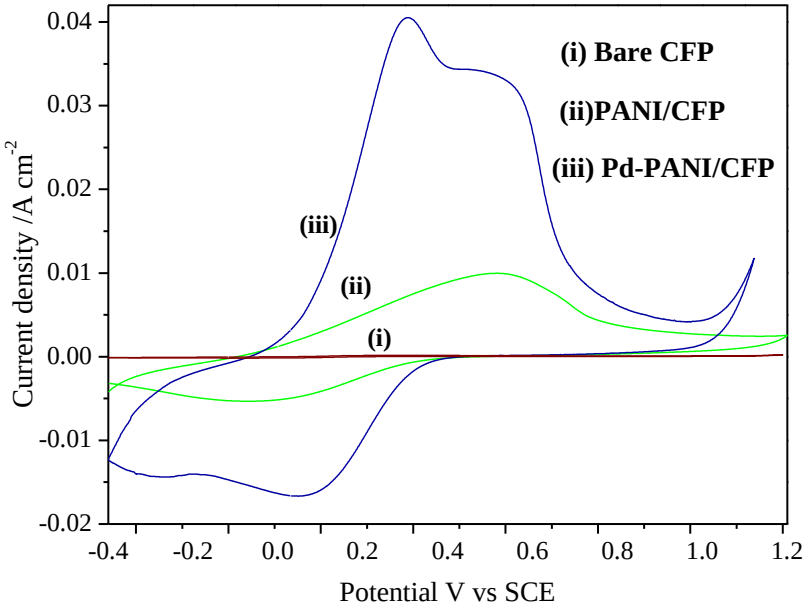


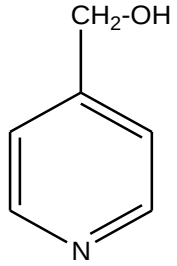
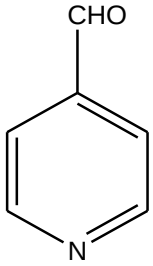
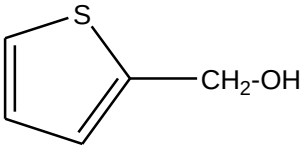
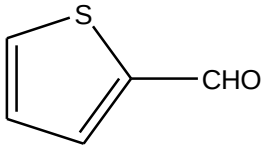
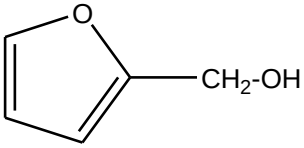
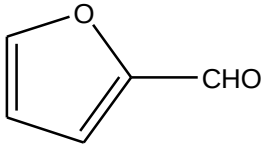
Figure 1. Cyclic voltammograms of 5 mM $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$at (i) Bare CFP, (ii) PANI/CFP and (iii) Pd-PANI/CFP in 0.1 M KCl.

The oxidation was performed between -0.4 V and 1.2 V at a scan rate of 0.05 Vs^{-1} in aqueous acidic medium in the presence of SDS. The oxidation of TEMPO begins around 0.1562 V at Pd-PANI/CFP, PANI/CFP and bare CFP electrodes whereas at 0.5501 V oxidation is achieved as a result of one-electron oxidation of nitroxyl radical to oxoammonium ion. The mediator TEMPO exhibits noticeable redox peaks at 0.3557 V and 0.6014 V (oxidation, i_{pa} = 0.2054 Acm^{-2} and i_{pa} = 0.0199 Acm^{-2} respectively) and 0.2229 V (reduction, i_{pc} = -0.0206 Acm^{-2}) at Pd-PANI/CFP electrode whereas it shows redox peaks of lower current density at PANI/CFP (oxidation at 0.3176 V and 0.5347 V, i_{pa} = 0.0166 Acm^{-2} and i_{pa} = 0.0177 Acm^{-2} respectively; reduction at 0.4173 V, i_{pc} = -0.0166 Acm^{-2}) and bare CFP (oxidation at 0.2435 V, i_{pa} = 0.0003 Acm^{-2}; reduction at 0.1357 V, i_{pc} = 0.0092 Acm^{-2}) electrodes. The oxidation of TEMPO becomes irreversible in the presence of pyridyl carbinol.

Different kinds of heterocyclic methanols are effective in electrocatalytic oxidation by using modified Pd-PANI/CFPelectrode. The choice of heterocyclic alcohols and the corresponding

aldehydes with yield are summarized in **Table 1**. Electrooxidation of 4-pyridyl carbinol at Pd-PANI/CFP composite electrode gives high current density with good yield compared to 2-thiophene methanol and 2-Furfuryl alcohol.

Table 1. Preparation of heterocyclic aldehydes from heterocyclic alcohols by using Pd-PANI/CFP electrode with TEMPO mediator.

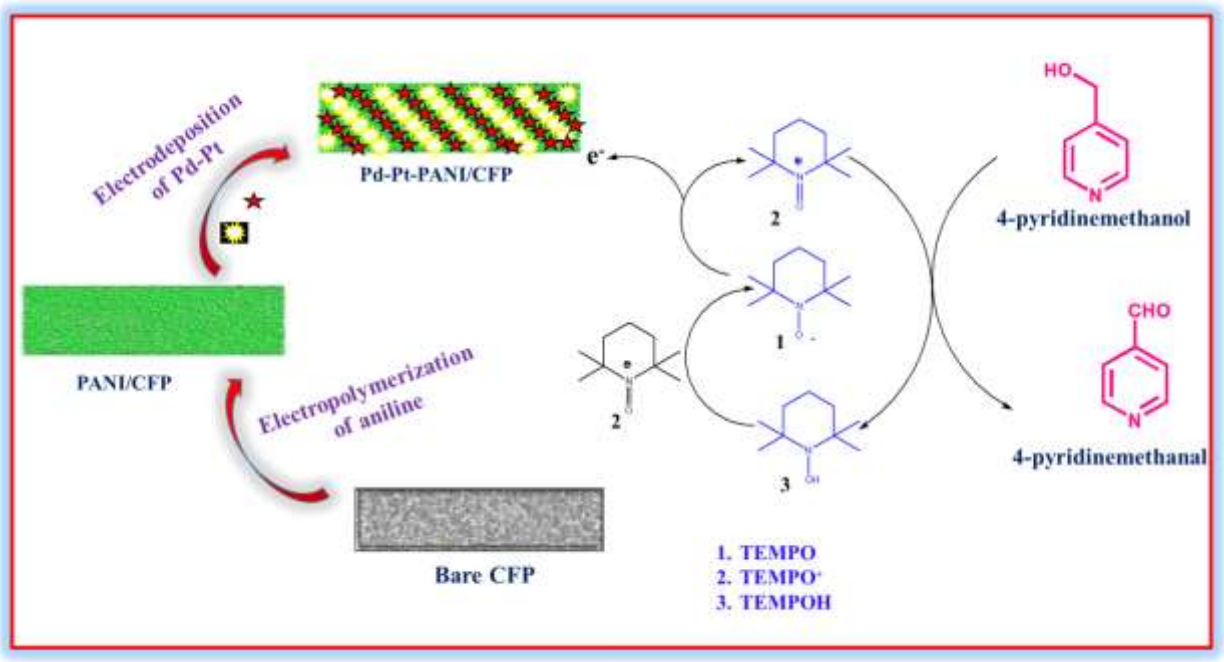
Entry (No)	**Reactant (Alcohol)**	**Electrode**	**Product (Aldehyde)**	**Yield (%)**
1	 4-pyridyl carbinol	Pd-PANI/CFP	 4- pyridyl carboxaldehyde	82
2	 2-thiophene methanol	Pd-PANI/CFP	 2-thiophene carboxaldehyde	74
3	 2-Furfuryl alcohol	Pd-PANI/CFP	 2-Furfuryl carboxaldehyde	76

I. Work 2 –Pd And Pt Co-Deposited polyaniline Modified Carbon Fiber Paper for TEMPO Mediated Electrochemical Oxidation of alcohols

Bimetallic nanoparticles (NPs) containing two different metals have increased electrocatalytic activity and chemical stability, water-insolubility, excellent electronic conductivity, controllable shape and size in comparison with monometallic ones. The catalytic properties of the original

single-metal catalysts can be improved by bimetallic nanoparticles as they can retain the functional features of each component exhibiting significant properties such as increased surface area, promoted electron transfer, and enhanced electrocatalytic activity due to the synergistic effects via cooperative interactions. Electrochemical methods are successfully used for the polymerization of conducting polymers on the carbon substrate, and three-dimensional growth on a substrate offers roughness and high porosity to the electrode.

This work illustrates the synthesis of PANI supported metal (Pd, Pt) nanoparticles on carbon fiber paper electrode (Pd-Pt/PANI/CFP) using the electrochemical co-deposition method, which exhibits exceptional monodispersity. The electrochemical properties of fabricated multi-layered films on carbon fiber paper (Pd-Pt/PANI/CFP) were investigated by electrochemical AC impedance spectroscopy and cyclic voltammetry (CV). FTIR, XRD, and XPS characterization technics were environmentally benign and sustainable are used to analyze the structural properties of the modified multi-layered electrode. The relative size of the metallic nanoparticles and their distribution on the electrode surface was analyzed using SEM and optical profilometry characterization techniques. We have also established their performance by utilizing them in the electrocatalytic oxidation of 4-pyridinemethanol as the model compound in aqueous acidic media. In particular, the synthetic parameters for Pd-Pt/PANI/CFP electrode were optimized to attain high electrocatalytic activity, and stability over a wide potential range for TEMPO mediated electrooxidation of 4-pyridinemethanol to 4-pyridinemethanal. The developed method is facile, highly efficient, cost-effective, and can be scaled up easily. Uniform distribution of palladium-platinum nanoparticles is facilitated by the presence of PANI host matrix. Electrochemical studies by CV showed that the Pd-Pt/PANI/CFP electrode had better electrochemical activity compared to PANI/CFP and Bare CFP electrode towards extensive electrochemical oxidation of 4-pyridinemethanolin presence of TEMPO in aqueous acidic medium. The Pd-Pt/PANI/CFP electrode has been successfully applied for the TEMPO-mediated electrocatalytic oxidation of 4-pyridinemethanol in an aqueous acidic medium. The illustration of the proposed work is schematically represented in **Scheme 2**.



Scheme 2. Schematic representation of the proposed Pd-Pt/ PANI/CFP composite electrode for electrocatalytic oxidation of 4-pyridinemethanol in TEMPO medium.

Electrochemical impedance spectroscopy (EIS) studies were applied to monitor the whole process of the preparation of modified electrodes and the charge transfer processes at the electrode-electrolyte interface. The impedance changes on the electrode surface between each step were analyzed by using these studies. **Figure 2** shows the representative Nyquist plots of EIS for the bare CFP, PANI/CFP, and finally modified Pd-Pt/PANI/CFP electrodes in the presence of equimolar 5 mM $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ taken in 0.1 M KCl (supporting electrolyte). The graphs obtained from EIS analysis contain a linear part and a semicircular part. The electron transfer limited process due to the porosity of the electrode corresponds to the semicircular part at higher frequencies, and the diameter is equivalent to the electron transfer resistance (R_{ct}). The diffusion-controlled doping and undoping of anions that result from Warburg behavior correspond to the linear part at the low-frequency end [45]. During the modification of electrodes, significant differences were observed. R_{ct} of the bare CFP is 98.6 Ω (**Figure 2, curve i**). The semicircle part in Nyquist plots is due to the charge-transfer resistance and the double-layer capacitance. Here, as we expected, the R_{ct} of the PANI/CFP electrode is smaller than that of the bare CFP. After CFP was modified with conducting polymer PANI, R_{ct} decreased to 62.8 Ω (**Figure 2, curve ii**), which is attributed to the electronic conducting pathway formed between the electrode and the electrolyte

solution. The results for the electrodes modified with Pd and Pt nanoparticles are shown in **Figure 2 (curve iii**); R_{ct} was further decreased to 27.3 Ω which confirms the increased conductivity in the modified electrode. The charge-transfer resistance (R_{ct}) of bare and modified electrodes were evaluated by fitting the electrical impedance spectra using the equivalent circuit (**inset of Figure 2**), and follow the order: R_{ct} (Pd-Pt-PANI/CFP) < R_{ct} (PANI/CFP) << R_{ct} (bare CFP) indicating the electronic coupling and improvement in the electrical conductivity of the electrode. The results show that the Pd and Pt nanoparticles and PANI film were successfully electrodeposited and polymerized on the CFP electrode surface.

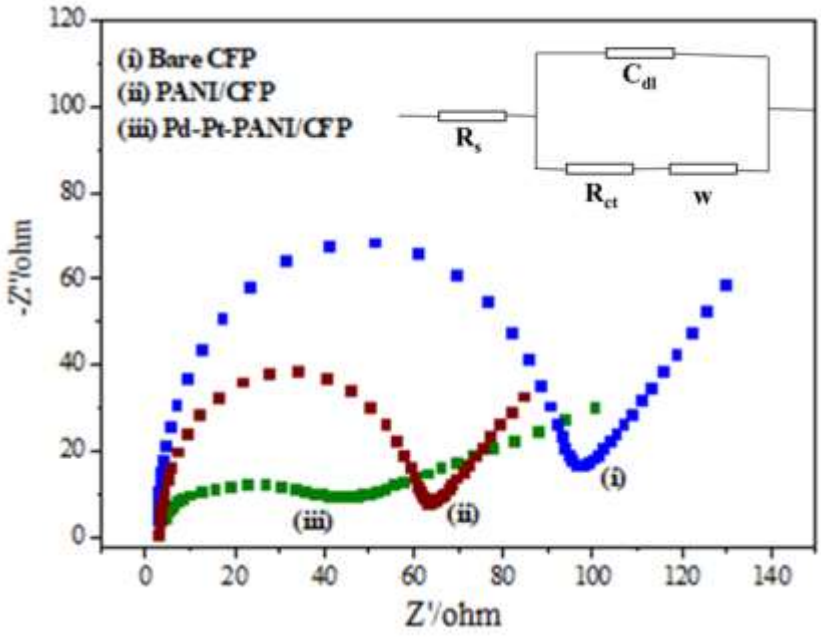


Figure 2. Nyquist plots of EIS in 5 mM $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ with 0.1 M KCl for bare CFP and modified electrodes, the inset is the equivalent circuit.

Figure 3 shows the cyclic voltammograms obtained from CV experiments to investigate the electrocatalytic oxidation of 4-pyridinemethanol at the bare CFP, PANI/CFP, and Pd-Pt/PANI/CFP electrodes. The electrochemical oxidation of 4-pyridinemethanol was carried out at a scan rate of 0.05 Vs^{-1} in TEMPO medium with a potential range between -0.8 and 1.2 V vs SCE, in aqueous solutions of 0.01 M H_2SO_4. No characteristic peak was observed in aqueous sulphuric acid. In addition to 0.01 M TEMPO solution to the reaction medium, a significant redox peak was observed at 0.4411 V and 0.5022 V as shown in **Figure 3a**, which could be attributed to the transfer

of an electron from TEMPO forming $TEMPO^+$. The peak current densities of Pd-Pt/PANI/CFP electrodes were found to be (-1.9472×10^{-4} A/cm^2 and 1.4579×10^{-4} A/cm^2 as shown in **Figure 3a (curve iii).** On adding 4-pyridinemethanol (10 mM) to the reaction medium, the peaks were shifted towards negative potential, -0.3994 V and 0.1291 V (**Figure 3b**); the corresponding peak current was increased to -0.0271 A/cm^2 and 0.0159 A/cm^2 for the finally modified electrode **(Figure 3b, curve iii)**. Oxidation of TEMPO becomes irreversible after the addition of 4-pyridinemethanol and the redox peak potential changed to a negative potential, appears wavy and broad (**Figure 3b**). The current density response for bare CFP and PANI/CFP electrodes is weak when compared to Pd-Pt/PANI/CFP electrode. **Figure 3c** shows the clear picture of the comparison of CV and the potential shift obtained for the Pd-Pt-PANI/CFP electrode (**Figure 3c, curve i**) in the absence and (**Figure 3c, curve ii**) presence of 4-pyridinemethanol.

TEMPO as a mediator converts primary -OH groups selectively to the corresponding carboxaldehydes. The real oxidation reagent is the nitrosonium ion ($TEMPO^+$) which is obtained by disproportionation of TEMPO in acid medium. In the oxidation of 4-pyridinemethanol, the $TEMPO^+$ is reduced to hydroxylamine (TEMPOH). TEMPO is regenerated from the hydroxylamine compound, TEMPOH, which is formed by the reduction of $TEMPO^+$ in a $2e^-$ transfer process at the electrode surface. After 48 hours, the reaction mixture was extracted with ethyl acetate; the product is isolated using column chromatography and confirmed by FTIR and ^{1}H NMR spectroscopy.

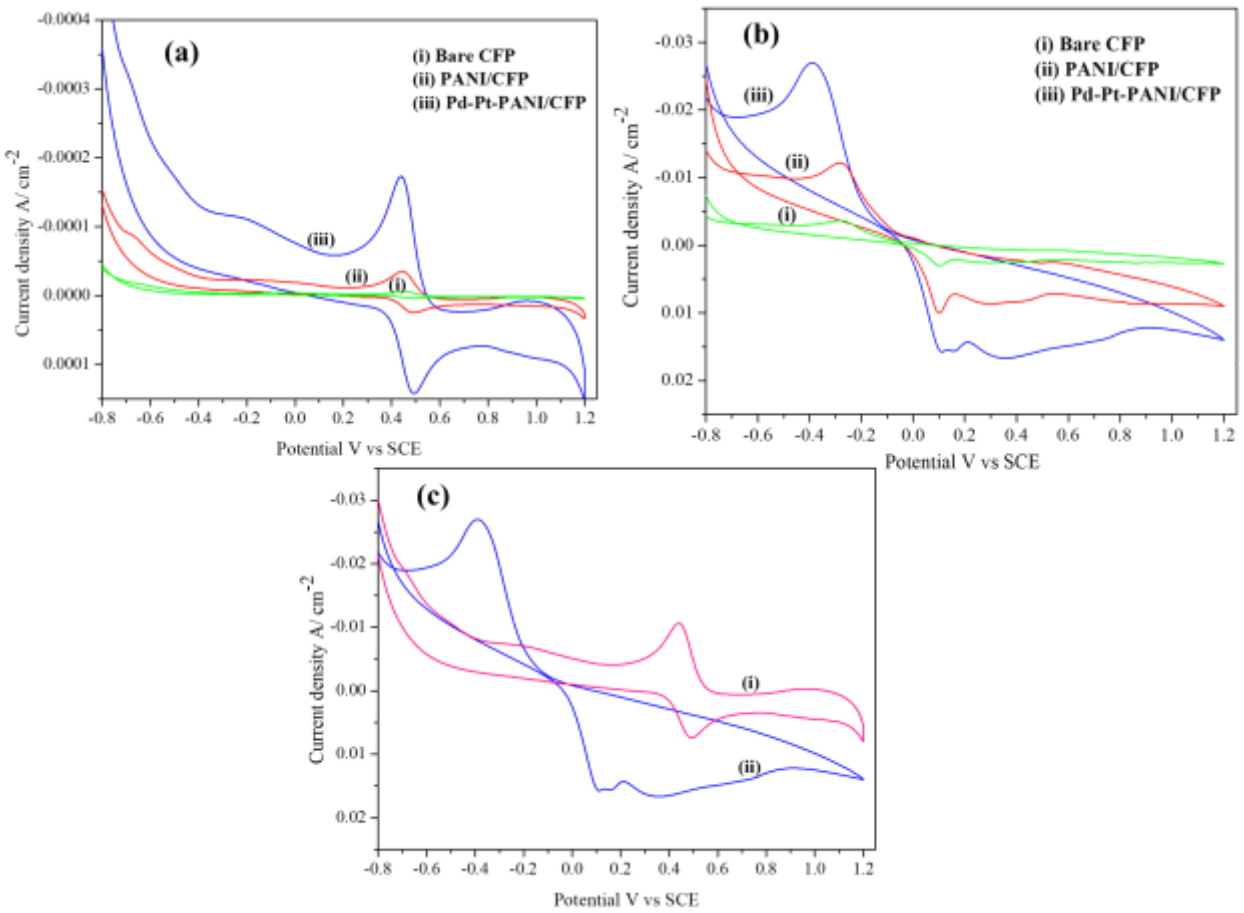


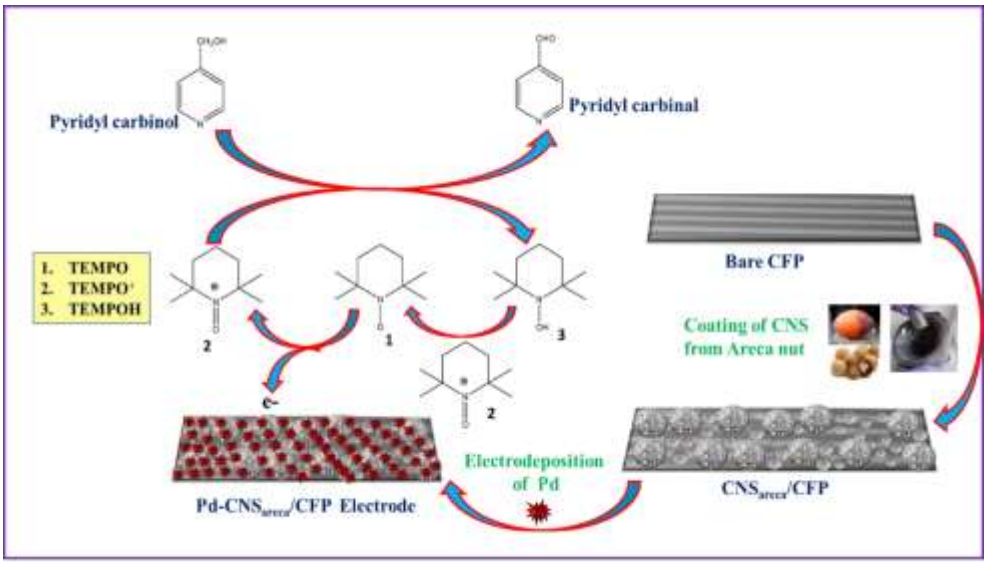
Figure 3. Cyclic voltammograms obtained for 0.01 M TEMPO in 0.01M H_2SO_4 at a scan rate of 0.05 Vs^{-1}, **(a)** in the absence of 4-pyridinemethanol **(b)** in the presence of 10 mM 4-pyridinemethanol in the acid medium, **(c)** comparison of CV obtained for Pd-Pt/PANI/CFP electrode (i) in the absence and (ii) presence of 4-pyridinemethanol

The one-step preparation of heterocyclic aldehydes from the corresponding heterocyclic alcohols by using Pd-Pt/ PANI/CFP composite electrode in TEMPO medium is observed. 4-Pyridinemethanol was efficiently converted to their corresponding 4-Pyridinemethanol with a yield of 80%. 2-Thiophenemethanol and 2-Furanmethanol electrochemically converted to 2-Thiophenemethanol (78 %) and 2-Furanmethanol(80 %) respectively.

II. Work 3- Surface modification of carbon fiber paper using Pd nanoparticles dispersed on biomass-derived porous nanoparticles for effective oxidation of heterocyclic carbinols

Metal nanoparticles dispersed on electrically conducting substrates have received considerable attention for applications as biosensors, electrochemical capacitors, anticorrosive coatings, and electrocatalysts. Carbon-based supports are generally used for dispersing the nanoparticles to achieve high catalytic activity. In this regard, CNSs can be used as an effective substitute to the carbon supports like graphene, carbon nanotubes, owing to their uniform dispersive ability on the electrode substrate and their porous nanostructures that can attract organic molecules towards the electrode surface. Carbon nanospheres (CNSs) derived from Areca catechu was coated on carbon fiber paper (CFP), decorated with Pd nanoparticles was employed for electrooxidation of pyridyl carbinol in an aqueous acidic medium. An environmentally benign and economic strategy was utilized for the preparation of CNSs obtained from Areca catechu. The physico-chemical characterizations and chemical composition of the modified electrode were studied using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) spectroscopy, and X-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM) techniques were used for analyzing the morphology of modified electrodes. The electrochemical characterizations of the modified electrodes were performed by Cyclic voltammetry (CV) and Electrochemical impedance spectroscopy (EIS).

In the present investigation, excellent electrocatalytic activity of Pd nanoparticles dispersed on CNS film coated carbon fiber paper (CFP) electrode was demonstrated for TEMPO mediated electrooxidation of heterocyclic carbinols in an aqueous acidic medium. The study was initiated by an investigation of electrooxidation of various kinds of heterocyclic carbinols with Pd nanoparticles dispersed on CNS_{areca}/CFP electrode in TEMPO medium. Pyridyl carbinol is taken as the model compound in this work for further studies. The reported methods in the literature generally involve multiple steps [41] whereas the present method follows a single-step for the deposition of Pd nanoparticles on CNS_{areca}/CFP to form a stable nanocomposite modified electrode. The process is facile, less expensive, and can be scaled up easily. The proposed work is schematically illustrated in **Scheme 3**.



Scheme 3. Schematic illustration for electrooxidation of pyridyl carbinol at Pd-CNS_{areca}/CFP composite electrode using TEMPO as a mediator.

CV was performed to investigate TEMPO-mediated electrocatalytic oxidation of pyridyl carbinol at Pd-CNS_{areca}/CFP, CNS_{areca}/CFPANId bare CFP electrodes (**Figure4**). The electrochemical oxidation was carried out in an aqueous acidic medium in the presence of 0.1 M H_2SO_4 and DW at a scan rate of 0.05 Vs^{-1}. In the cyclic voltammogram obtained for Pd-CNS_{areca}/CFP electrode in aqueous sulphuric acid, no characteristic peak was observed. On adding 0.01 M TEMPO solution to the above reaction medium, a characteristic redox peak appeared at 0.432 V and 0.496 V as shown in **Figure 4a**. To the reaction medium mentioned above, on adding pyridyl carbinol, TEMPO peak was observed to shift towards the potential negative to that obtained for TEMPO oxidation in the absence of pyridyl carbinol and the peaks appeared to be broad and wave-like (**Figure 4b**). The cyclic voltammograms recorded for the oxidation of TEMPO in the absence of pyridyl carbinol display the low current response in the case of bare CFP electrode and CNS_{areca} modified CFP electrode, whereas a broad cyclic voltammogram was obtained for Pd-CNS_{areca} modified CFP electrode as seen in **Figure 4a**. The redox peaks were obtained at about 0.505 V (reduction) and 0.433 V (oxidation) in the presence of 0.01 M TEMPO, which corresponds to one-electron transfer from TEMPO to $TEMPO^+$. TEMPO oxidation becomes irreversible in the presence of pyridyl carbinol. The redox peaks shifted to reduction around 0.549 V and oxidation at 0.014 V is less pronounced and appears wavy and broad when compared to the peaks obtained

for TEMPO oxidation in the presence of pyridyl carbinol (**Figure4b**). TEMPO in the presence of pyridyl carbinol gives a weak current response for bare CFP and CNS_{areca}/CFP electrodes when compared to Pd-CNS_{areca}/CFP electrodes. Pyridyl carbinol oxidation mediated by TEMPO results in the formation of pyridyl carbinal at Pd-CNS_{areca}/CFP electrode and the product mixture was extracted with ethyl acetate and concentrated in a rotary evaporator and purified by column chromatography. The products were analyzed and confirmed by ^{1}H NMR and FTIR spectroscopy and the isolated yield was 84%.

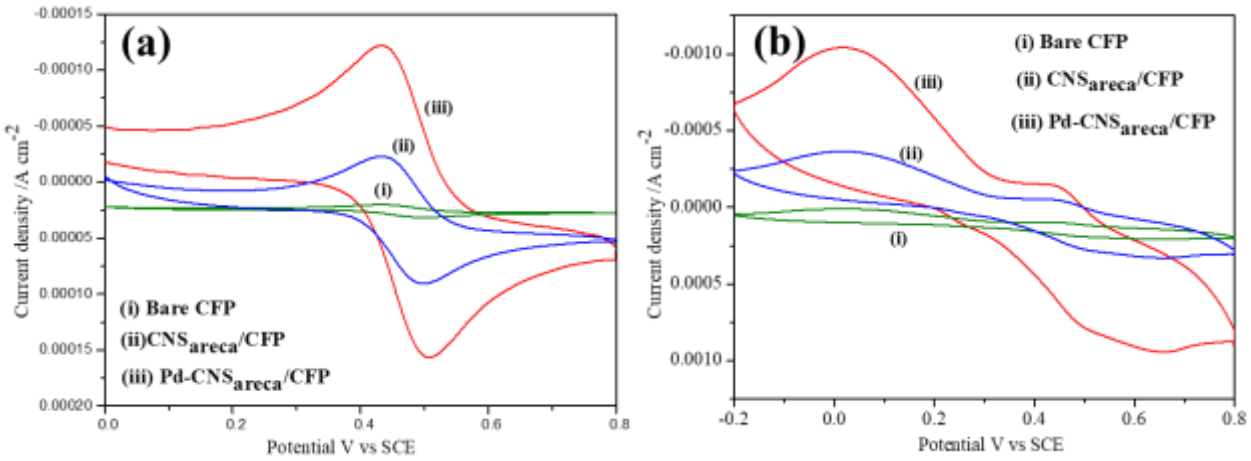


Figure 4.(a) Cyclic voltammograms of 0.01 M TEMPO at (i) bare CFP (ii) CNS_{areca}/CFP and (iii) Pd-CNS_{areca}/CFP in the absence of 10 mM pyridyl carbinol with 0.1 M H_2SO_4 in aqueous medium, scan rate (0.05 Vs^{-1}) **(b)** Cyclic voltammograms of 0.01 M TEMPO at (i) bare CFP (ii) CNS_{areca}/CFP and (iii) Pd-CNS_{areca}/CFP in the presence of 10 mM pyridyl carbinol with 0.1 M H_2SO_4 in aqueous medium at room temperature (303 K) with scan rate 0.05 Vs^{-1}.

III. Work 4 - MnO_2-Pi on Biomass Derived nanocarbon spheres for Electro-Catalytic Oxidation of Heterocyclic Carbinol on carbon fiber paper electrode

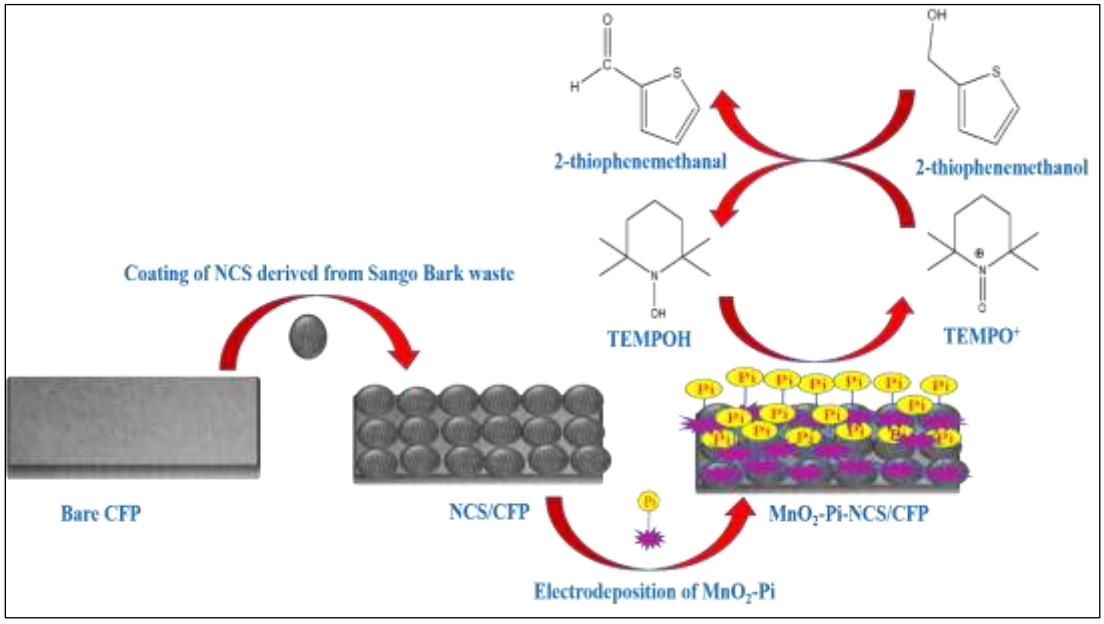
Carbon-based materials such as charcoal, activated carbon, carbon nanotubes, carbon nanofibers, fullerenes, graphene, and porous nanocarbons are receiving significance due to low density, large surface area, good flexibility, high mechanical strength, and stability. Among carbon-based materials, the nanocarbon spheres (NCS) exhibit distinguishing advantages, like simple preparation methods, uniform particle size, consistent surface morphology, larger porosity, and specific surface area, good dispersity, higher chemical, and thermal stability, excellent biocompatibility, larger ionic and electronic conductivities, and higher packing density, when

compared to the other forms of carbons. NCS has been used as the substrate for electrode materials in the manufacture of polymer electrolyte membrane fuel cells [19], energy storage devices, such as supercapacitors.

The general methods of synthesizing NCS include arc discharge, chemical vapor deposition (CVD), nano-casting, hydrothermal carbonization of sugars, and polymeric aerogels. But these methods follow harsh synthetic conditions and demand large consumption of energy. Therefore, in this work, NCS is prepared from Sago bark waste in a clean, environmentally friendly, catalyst-free, and economically favorable one-pot pyrolysis process.

MnO_2 nanoparticles are typical transition-metal oxides which are considered to be one of the most promising metal oxides due to abundant reserves, environmentally benign nature, and low toxicity, low cost, and excellent electrochemical performances [78]. Electrodeposition of metal ions such as Mn^{2+} in phosphate buffer solutions on substrate electrodes contained substantial amounts of anions from the buffer medium. Such materials are clusters of interrelated metal-oxo/hydroxocubanes with terminal ligation to the electrolytic species. These catalysts can operate under neutral or near-neutral pH conditions and have displayed long-term catalytic activity [79,80]. The excellent electrocatalytic activity of Manganese oxide-Phosphate (MnO_2-Pi) dispersed on NCS derived from *sago barks* coated carbon fiber paper (CFP) electrode is utilized for electrocatalytic oxidation of heterocyclic carbinols. In the present study we have taken 2-thiophenemethanol as the model compound for further studies and schematically represented in **Scheme 4**. The wastes of Sago bark were used as raw material for the preparation of porous NCS. MnO_2-Pi nanoparticles were electrochemically deposited on NCS coated CFP electrode from 0.1 M phosphate buffer solution (PBS, PH 7.0), containing 20 mL of 0.025 M $KMnO_4$. The electrodeposition of MnO_2-Pi nanoparticles on NCS/CFP electrode was performed in the potential range -0.1 to 0.6 V at a sweep rate of 0.05 Vs^{-1} up to 25 cycles. Different analytical methods were used to characterize the modified electrodes. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to study the electrochemical properties of the modified electrodes. The electrochemically active surface area values calculated for bare CFP, NCS coated CFP and MnO_2-Pi-NCS/CFP electrodes were found to be 1.43 cm^2, 2.86 $cm^{2,}$ and 6.72 cm^2 respectively for the geometric area of 0.7 cm^2 of the electrodes. Coating of NCS and MnO2-Pi resulted in porosity and roughness of CFP electrode which enhances the surface area.

In the current study, MnO_2-Pi nanoparticles scattered on the NCS layer coated carbon fiber paper (CFP) electrode are applied for the electrocatalytic oxidation of 2-thiophenemethanol to 2-thiophenemethanal, in a TEMPO mediated acidic medium. The methods reported, so far, regarding the oxidation process include several steps; whereas, the present work introduces a novel method of oxidizing 2-thiophenemethanol in one step, using MnO_2-Pi based solid nanocomposite modified electrode. This method can be scaled up easily due to its facile nature and low-cost. Schematic illustration of the current work is represented in **Scheme 4**.



Scheme 4. Schematic illustration for the application of MnO_2-Pi-NCS/CFP electrode, for electrocatalytic oxidation of 2-thiophenemethanol.

Cyclic voltammetric experiments were conducted to investigate the electrocatalytic oxidation of 2-thiophenemethanol at the bare CFP, NCS/CFP, and MnO_2-Pi-NCS/CFP electrodes (**Figure 5**). The study was conducted at a scan rate of 0.05 Vs^{-1} in TEMPO medium with a potential range between -0.6 and 0.8 V vs SCE, in solutions of 0.01 M H_2SO_4. No characteristic peak was observed in the cyclic voltammograms obtained for the bare and modified CFP electrodes. But when TEMPO solution (0.01 M) was added to the above reaction medium, redox peaks were appeared at 0.4491 V and 0.5283 V, which could be attributed to the transfer of an electron from TEMPO forming $TEMPO^+$; the peak currents of bare CFP, NCS/CFP and MnO_2-Pi-NCS/CFP

were found to be (-8.479 x 10^{-6} A/cm^2 and 1.155 x 10^{-5} A/cm^2), (1.77 x 10^{-5} A/cm^2 and 2.269 x 10^{-5} A/cm^2) and (-5.3535 x 10^{-5} A/cm^2 and 7.1613 x 10^{-5} A/cm^2), respectively, as shown in **Figure 5a**. On adding 2-thiophenemethanol (10 mM) to the reaction medium, the peaks were shifted towards negative potential, -0.3631 V and 0.2533 V (**Figure 5b**); the corresponding peak current was increased to -0.00128 A/cm^2 and 0.02009 A/cm^2 for the finally modified electrodes. The results indicate a marginally small current flow through bare CFP and NCS/CFP electrodes (**curves i** and **ii**). At MnO_2-Pi-NCS/CFP electrode, the high energy active sites of MnO_2-Pi nanoparticles attract substrate molecules largely towards the electrode surface, leading to increased electron transfer kinetics and higher current flow (**curve iii**). Molecules of 2-thiophenemethanol were greatly attracted toward the electrode surface.

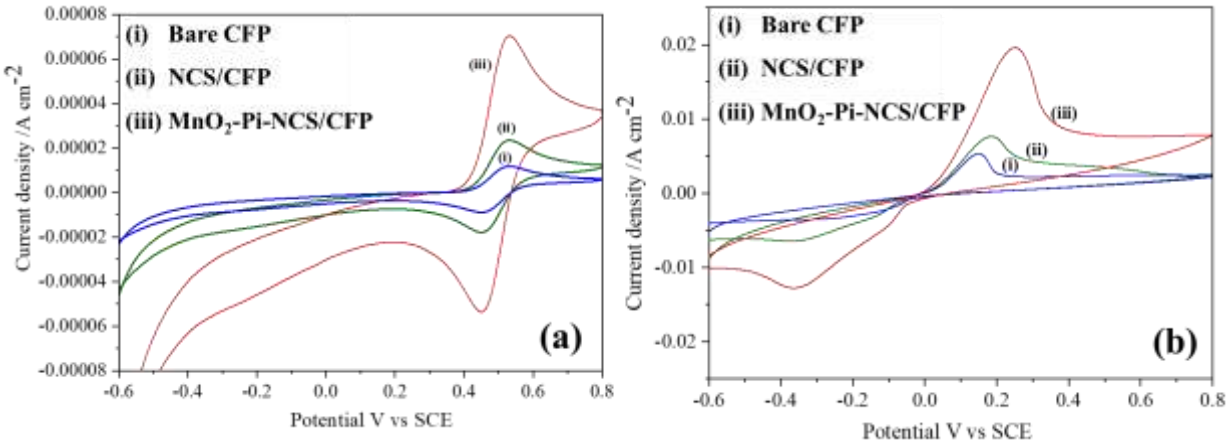


Figure 5. Cyclic voltammograms obtained for 0.01 M TEMPO in 0.01M H_2SO_4at scan rate of 0.05 Vs^{-1}, **(a)** in the absence of 2-thiophenemethanol **(b)** in the presence of 10 mM 2-thiophenemethanol in the acid medium

The conversions of different heterocyclic carbinols to their corresponding heterocyclic aldehydes are studied. Good to excellent yields of the products were obtained for electrooxidation of alcohols by using MnO_2-Pi-NCS/CFP composite electrode. 4-pyridyl carbinol and 2-thiophene methanol, 2-Furan carbinol gave yields of 80%, 82% and78% respectively in these oxidation reactions.

2. Conclusions

The application of electrochemical methodologies to organic synthesis is receiving significant attention from industry and research centers worldwide, not only because transformations can

often be conducted more efficiently, but also because electrochemical processes can decrease pollution and make the chemistry environmentally friendly. Electroorganic chemistry has enhanced the synthetic possibilities of academic and industrial ventures. It has a wide range of applications in various organic synthetic techniques based on the electrocatalytic activity of modified substrates.

In the present study, the use of TEMPO mediator has broken the barrier and changed the experimental setup to a much more environmentally benign way. Modified electrodes were used here for the electrooxidation of heterocyclic carbinols and their derivatives into corresponding aldehydes. The proposed method is more advantageous over other reported methods, by its high selectivity in the oxidative conversion of carbinol to carbinal. The maximum yield was achieved in a single-step reaction at an ambient temperature and pressure. The transition metal-free TEMPO mediator makes the present method more environmentally benign. Maximum current efficiency is maintained throughout the experiment and the percentage yield was found to increase gradually with an increase in the charge passed through the cell. The products obtained were purified and characterized by different spectroscopic techniques.

The electrocatalytic efficiency was explored by dispersing palladium, MnO_2, platinum in nanomolar level on PANI host matrix and CNSs which is coated on CFP. The nanostructure morphology of Pd, Pt, and MnO_2-Pi was found to be uniformly dispersed on the surface of the electrode. Electrocatalytic activity of modified Pd-PANI/CFP, Pd-Pt/PANI/CFP, Pd-CNS_{areca}/CFP, and MnO_2-Pi-NCS/CFP electrode towards the oxidation of heterocyclic carbinols such as pyridyl carbinol, thiophene methanol, and furfuryl in presence of TEMPO in aqueous acidic medium was studied using cyclic voltammetry. The electrochemically deposited nanoparticles act as high energy surface sites in attracting the molecules of carbinols towards the electrode surface and provide channels for the same to diffuse into the conducting polymer matrix. The modified electrode was characterized by Raman, FTIR, XRD, XPS, SEM, TEM, and electrochemical analysis. EIS studies revealed that all modified carbon fiber paper electrodes (Pd-PANI/CFP, Pd-Pt/ PANI/CFP, Pd-CNS_{areca}/CFP, and MnO_2-Pi-NCS/CFP) enhance conductivity towards the electrocatalytic oxidation of heterocyclic carbinols. Direct oxidation of heterocyclic carbinols to corresponding heterocyclic carbinals with high selectivity and good yield could be achieved in a single step using the proposed method.

The thesis will be divided into seven chapters. Chapter 1 will be the introduction chapter. Chapter 2 describes the review of literature, which will cover the significant reported works for electrode modification and the need for electrocatalytic oxidation of heterocyclic carbinols. Chapter 3 describes the electrocatalytic oxidation of heterocyclic carbinols on electrodeposited Pd-PANI/CFP electrodes. Chapter 4 will be based on dispersed Pd-Pt nanoparticles on PANI coated carbon fiber paper for the electrochemical oxidation of alcohols. Chapter 5 is the Surface modification of carbon fiber paper using Pd nanoparticles dispersed on biomass-derived porous nanoparticles for effective oxidation of heterocyclic carbinols. Chapter 6 focuses on MnO_2-Pi on Biomass Derived nanocarbon spheres for Electro-Catalytic Oxidation of Heterocyclic Carbinol on carbon fiber paper electrode. Chapter 7 briefs on the conclusions of the research work and this is followed by details on paper publications and conference proceedings.

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Publications and proceedings

1. Papers in journals

[1] Agnus T. Mathew, K. B. Akshaya, T. P. Vinod, Anitha Varghese, * and Louis George, *TEMPO-Mediated Aqueous Phase Electrooxidation of Pyridyl carbinol at Palladium-Decorated PANI on Carbon Fiber Paper Electrode*, ***ChemistrySelect (***2020), 5, 3283 – 3294.

[2] Agnus T. Mathew, Vinay S. Bhat, S. Supriya, T. Maiyalagan, Anitha Varghese, and Gurumurthy Hegde. "TEMPO mediated electrocatalytic oxidation of pyridyl carbinol using palladium nanoparticles dispersed on biomass derived porous nanoparticles." ***Electrochimica Acta*** 354 (2020): 136624.

[3] Agnus T Mathew, S. Supriya; Akshaya K B; Kannan Perumal,; Anitha Varghese, Gurumurthy Hegde MnO2-Pi on biomass derived porous carbon for electro-catalytic oxidation of pyridyl carbinol". ***Journal of the electrochemical society(2020)***

[4] Agnus T Mathew, Supriya S, Akshaya K B, Anitha Varghese, Gurumurthy Hegde. "An aqueous phase electrocatalytic oxidation of 2-thiophenemethanol at MnO2-Pi dispersed nanocarbon spheres on carbon fiber paper electrode". ***RSC Advances***

2. Conference proceedings

[1] Poster presentation titled by "*Electrochemical oxidation of pyridyl carbinol mediated by TEMPO using Pd decorated PANI on carbon fiber paper electrode"* in iSAEST– 12 conference held during 08-10, January 2019 at Hotel Trident, Chennai, India.

[2] Poster Presentation of the research paper titled "*Conducting polymer decorated by Pd nanoparticles on carbon fiber paper electrode for Electrochemical oxidation of pyridyl carbinol in aqueous medium*" in the ICCM 2019 held during 17th -19th October 2019 at Mangalore University, Mangalagangothri, India.

[3] Poster Presentation of the research paper titled "*TEMPO mediated electrochemical oxidation of Benzyl alcohol by β-CD-PPy modified carbon fiber paper electrode***"** in the NCE-21 held during 30th -31st January 2020 at VIT, Chennai, India.

[4] Poster Presentation of the research paper titled "*Polyaniline decorated by Pd nanoparticles on carbon fiber paper electrode for Electrochemical oxidation of pyridyl carbinol mediated by TEMPO in aqueous acidic medium*" in the PPCS-2020 held during 15th Feb 2020 -15th March 2020 at Christ University (Deemed to be University),Bangalore, India.

[5] Poster Presentation of the research paper titled ***"****Electrochemically decorated MnO_2-Pi on biomass derived porous carbon modified carbon fiber paper for electro-catalytic oxidation of pyridyl carbinol****"*** in the VI J-NOST held during 31st Oct 2020 -1st Nov 2020 at Indian Institute of Science, Bangalore, India.